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Transient CO adsorption and the catalytic properties of surfaces

M. Rocca,* L. Vattuone, L. Savio, F. Buatier de Mongeot, and U. Valbusa
Istituto Nazionale per la Fisica della Materia, and CFSBT-CNR, Dipartimento di Fisica, via Dodecaneso 33, 16146 Genova, Italy

G. Comelli
Laboratorio TASC INFM and Dipartimento di Fisica, Trieste, Italy

S. Lizzit, A. Baraldi, and G. Paolucci
Sincrotrone Trieste SpA, SS 14 Km 163,5 in Area Science Park 34012 Basovizza Trieste, Italy

J. A. Groeneveld and E. J. Baerends
Vrije Universiteit, Amsterdam, The Netherlands
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We show that in presence of subsurface oxygen, CO oxidation of oxygen precovered Ag(001) modifies the surface in such a way that CO adsorption is stabilized up to crystal temperatures of 160 K. When diffusion is activated new surface oxide phases form, characterized by oxygen both in surface and in subsurface sites and by a high density of states just below the Fermi level. Subsurface oxygen accumulation might therefore be relevant for the understanding of the origin of the pressure gap observed for ethylene epoxidation and other important catalytic reactions.

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Several important catalytic reactions work readily in industrial reactors but do not take place under controlled ultrahigh vacuum conditions (UHV).[1] The physical reason for the pressure gap was heavily debated over the past decades, but it is not yet assessed. Partial C_2H_4 oxidation on Ag powders is one of the most studied examples of reactions not occurring in UHV.[2] Ethylene oxide (EtO) was demonstrated to form on silver surfaces ''activated'' by annealing at high pressure in a reaction mixture of C_2H_4 and O_2 (Ref. 3) and more recently also of CO and O_2.[4] The nature of the surface modification produced by the pretreatment was not clarified. In the present paper we shall show that CO oxidation under UHV conditions modifies indeed the Ag surface in such a way that stable CO adsorption can occur even at crystal temperatures T of 160 K, while for the untreated surface such adsorbate is unstable already at $T=100$ K. The effect is caused by subsurface oxygen accumulation. When also diffusion is activated new phases with oxygen both in surface and in subsurface sites form, which are characterized by an enhanced density of states close to the Fermi level.

As demonstrated in a previous publication,[5] following dissociative O_2 adsorption three different oxygen moieties form on Ag(001), which are characterized by O($1s$) binding energies, $E_B[\mathrm{O}(1s)]$, of 528.3, 530.3, and 530.8 eV, and will therefore be referred to as O528, O530, and O531, respectively. O528 and O530 correspond to *adatom* species, while O531 consists of oxygen atoms in the very first *subsurface* layers. Photoelectron diffraction proved that O528 sits in the fourfold hollows of the unreconstructed surface, while O530 occupies the former fourfold hollows in the troughs of a missing row $2\sqrt{2}\times\sqrt{2}$ reconstructed substrate. The two phases are linked by a reversible phase transition just above room temperature. The low-temperature phase, O530, is thereby stabilized by the presence of O531. Only the O528 moiety is removed by CO or C_2H_4 oxidation, leading to total combustion.

The present measurements were performed at the SuperESCA beamline of the ELETTRA Synchrotron radiation facility in Trieste by x-ray photoemission spectroscopy (XPS). Details on the beamline can be found in Ref. 6. The O($1s$) region was investigated at a photon energy $h\nu$ of 650 eV and the C($1s$) region at $h\nu=430$ eV, in order to obtain comparable sensitivities to C and to O. For the valence band $h\nu=215$ eV was employed. The spectra were normalized to the secondary electron plus inelastic tail background at 30 eV below the Fermi level, E_F; they were recorded at an emission angle of 40° with respect to the surface normal and with plane polarized photons impinging at 80°. The same Ag(001) sample, oriented to within 0.25° off the nominal plane, was used in all experiments. It was prepared by sputtering and annealing cycles until a sharp (1×1) low-energy electron diffraction (LEED) pattern was obtained and no contaminants could be detected by XPS independently of the concentration of dissolved oxygen. The latter quantity is not easy to control by surface sensitive spectroscopies for its elusive nature, but we have evidence that it increased significantly by exposing the sample to atmospheric pressure for several months and that it could be depleted by prolonged sputtering and annealing cycles. In Fig. 1 we show the photoemission spectra measured in the O($1s$), in the C($1s$) and in the valence band region after dosing CO at $T=130$ K on a surface with both O528 and O530 (both oxygen species were necessarily present as O528 converts back to O530 below room temperature[5]). After the first 18 L ($1\ \mathrm{L}=10^{-6}$ torr $\times$s) of CO the peak at 528 eV has disappeared, while the intensity of the O530 feature is unchanged. The peak at 533.1 eV and the broad companion around 287 eV are in-

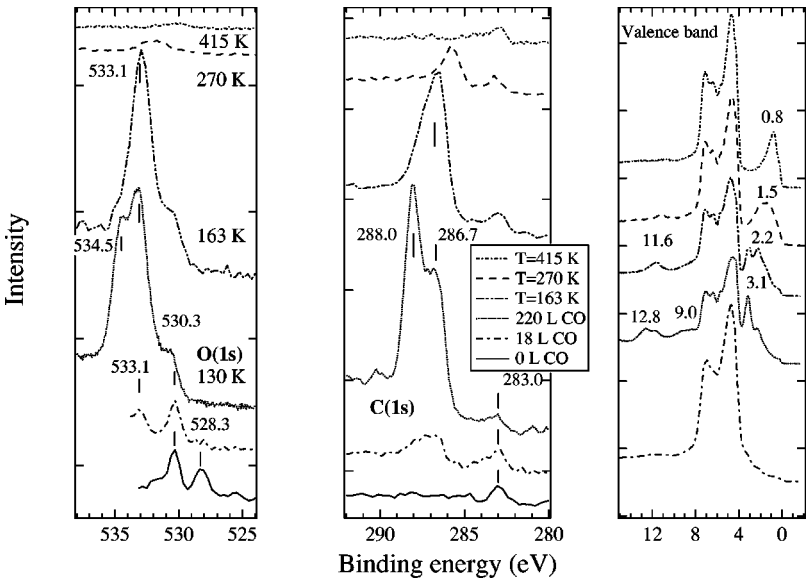

FIG. 1. XPS spectra of the O(1*s*) and C(1*s*) and valence-band regions obtained after CO exposure at 130 K of a dissolved oxygen rich sample covered with O528 and O530 (unreactive), showing the stabilization of CO adsorption after the removal of O528. When heating the sample CO desorption takes place and a peak develops below E_F.

dicative of CO adsorption. This phenomenon is unexpected since CO desorbs already at 65 K for clean Ag(110) (Ref. 7) and it is usually unstable for oxygen covered Ag(001) above $T=100$ K.[8] CO adsorption was occasionally reported in literature for 100 K$<T<$200 K (Refs. 8–10) but no explanation was provided for this intriguing effect. We note that our XPS peaks cannot be due to carbonates, as different binding energies and a higher decomposition temperature (see below) would be expected.[11] Upon further CO dosing two CO moieties with $E_B[C(1s)]=286.7$ eV and $E_B[0(1s)]=533.1$ eV and 288.0 eV and 534.5 eV, respectively, are present. Both E_B values are in the energy range of CO chemisorbed in the atop site.[12] In the valence band we find the expected CO peaks at $\approx$9 eV (5σ and 1π) and 12.8 and 11.6 eV (4σ), already reported for CO/Ag(110).[9,13] The peak at 3.1 eV, observed by Canepa *et al.*[9] working at $T=160$ K but not by Krause *et al.*[13] working at $T=50$ K (physisorbed CO), is indicative of CO chemisorption. The CO moiety with $E_B=288.0$ eV is unstable above 130 K, while the other desorbs for $T>163$ K, i.e., approximately 3 times higher than for CO on bare Ag(110). The residual intensity at 286 and 532 eV present at 270 K might be due to still another CO moiety.

Substantial stabilization of the CO admolecules must therefore have taken place. This effect is not associated to the mere presence of O530, since CO adsorption is not observed on oxygen precovered Ag(001) at $T=100$ K.[8] CO stabilization cannot be induced by O528 either, as CO sticks even after complete removal of this adatom species. The surface obtained after removal of O528 by CO is thus different from the clean surface and from the surface covered with O530 only. In spite of this striking difference in the chemical properties of these surfaces, their photoemission spectra are indistinguishable, except for the CO peaks. When annealing the crystal the CO related features disappear, indicating that CO desorbs, while the previously weak peak at 2.2 eV grows and broadens, shifting firstly to 1.5 eV at $T=270$ K and finally evolving into a sharp feature at 0.8 eV at $T=415$ K. After annealing to 415 K only a broad and weak feature at 530.5 eV, indicative of subsurface oxygen accumulation, is present. No contaminants are evidenced by XPS. No peak at E_F forms on the contrary when annealing an oxygen covered surface without previous CO dosing.

In Fig. 2 (left panel) we show the photoemission spectra for the valence band region for a CO oxidation experiment performed at $T=360$ K. Little intensity is present in the Ag(5*s*) region, i.e., between 4 eV and E_F, both for the clean and for the oxygen covered surface [about 0.1 monolayer (ML) coverage], except for the O(2*p*) antibonding state of O528 at 2 eV. We can see that 11 L of CO (dotted line in the inset) were sufficient to remove the O528 adatoms (solid line) and that after the exposure the overall photoemission intensity above the *d* bands is twice as large as for the bare surface (chained line). The corresponding XPS spectra for the O(1*s*) region show that another species with $E_B=529.0$ eV (O529) is generated, which is less reactive towards CO. Such species forms when *T* is high enough, as in the experiment at 130 K we only observed that O528 is removed. O529 cannot therefore be generated from O528. Upon further CO dosing the O(1*s*) peak broadens considerably and shifts towards 530.5 eV while in the valence band region a peak at 0.8 eV forms. The integrated intensity of the O(1*s*) peak is comparable to the one of the O528 peak before dosing CO. An quantitative estimate of the oxygen amount is however difficult as part of the signal arises from oxygen atoms located in subsurface sites. Dosing CO at $T=360$ K on O528 leads therefore to the same structure, containing subsurface oxygen atoms, obtained by dosing at 130 K and annealing. The C(1*s*) photoemission region, reported in the uppermost panel, remains unstructured, witnessing that the dynamical CO coverage is smaller than 10^{-3} ML. Again no contaminant could be detected by XPS. Since no oxygen is dosed with CO and since no CO dissociation takes place (otherwise C contamination would be significant), we conclude that the excess oxygen in subsurface sites must have segregated from the bulk. We notice that no oxygen accumulation in the subsurface region occurs in absence of CO as after exposing the sample to 86 000 L of oxygen at $T=470$ K, a temperature at which subsurface migration is efficient,[14]

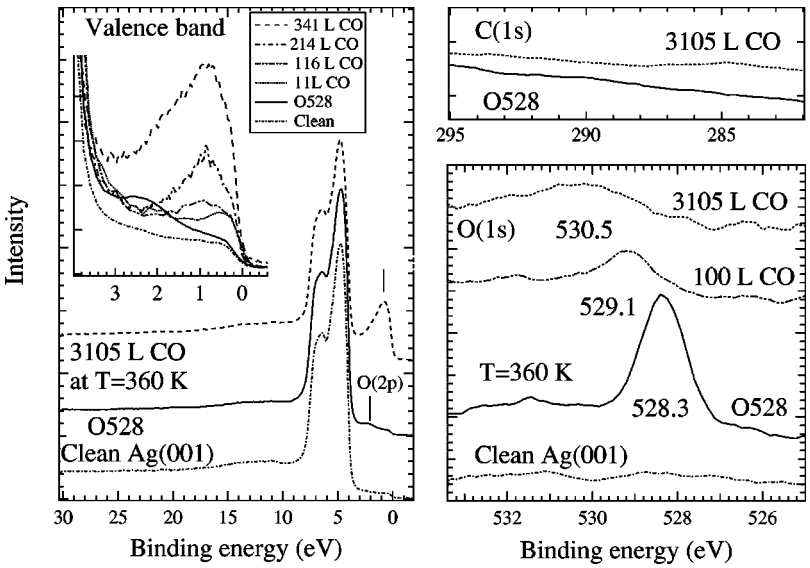

FIG. 2. XPS spectra of valence-band region (left panel) and O(1*s*) and C(1*s*) (right panels) recorded for CO exposure on O528 /Ag(001) at 360 K. From bottom up: clean surface, O528 covered surface (0.1 ML coverage) and after CO exposure. The region above the *d* bands is enlarged in the inset for clean (chained line) and oxygen covered (continuous line) surface cases and for CO doses of 11, 116, 214, and 341 L (from bottom up).

we observed only O528 related peaks and no intensity enhancement at E_F. Oxygen segregation is therefore promoted by transient CO adsorption.

In order to identify the relation between subsurface oxygen and the increased density of states (DOS) close to E_F, we computed the total DOS in the valence band region of Ag(001) slabs with 1 monolayer (ML) of oxygen in surface as well as in various subsurface sites. The code employed (ADF-BAND version 1999.03) was discussed elsewhere.[15] Since oxygen is only barely energetically stable in octahedral interstitial sites and unstable in tetrahedral sites, substantial vertical relaxation of the layers was applied, which considerably stabilizes subsurface oxygen. Compared to the DOS for bare Ag(001) [see Fig. 3(a)], the slabs with only either oxygen adatoms or oxygen in subsurface sites exhibit enhanced DOS between the top of the *d* band and E_F because of the formation of O(2*p*)-Ag(4*d*) antibonding states (not shown). In accord with literature,[16] the increase is however relatively weak at E_F, and stronger between 2 and 3 eV below E_F. According to Van den Hoek *et al.*,[21] enhancement of the DOS near to E_F can be obtained in presence of oxygen simultaneously in surface O_{ad} and subsurface O_{sub} sites because of the formation of an $O_{ad}(2p)$-$O_{sub}(2p)$ antibonding structure. However, we did not observe this effect for the Ag(001) geometry with O_{sub} in the octahedral site.

Stimulated by the DOS of bulk Ag_2O,[17] which exhibits a striking peak at 0.8 eV below E_F (the top of the valence band), see Fig. 3(b), we investigated the possible restructuring of the surface region with subsurface oxygen atoms placed in an Ag_2O-like structure. Calculations have been performed for a slab with four Ag layers and with oxygen in tetrahedral sites between the top layers in an Ag_2O-like arrangement, reported schematically in the inset of Fig. 3. Interlayer distances in the *z* direction have been relaxed for energetic stabilization and lattice distances in the *x* and *y* directions chosen conforming to the underlying Ag crystal (the DOS is however little sensitive to the relaxation of the lateral lattice parameters). The DOS of this surface oxide phase is still low near E_F, but it could be significantly increased in that region when adding also oxygen adatoms due to the formation of an $O_{ad}(2p)$-$O_{sub}(2p)$ antibonding structure with significant Ag(4*d*) character. The result, reported in Fig. 3(c), strongly resembles the spectrum measured in the early stages of the CO exposure experiment (see dotted and dot-dot-dashed spectra in the inset of Fig. 2), although one should keep in mind that photoemission intensity and DOS are not necessarily proportional, being related by state dependent matrix elements. We notice also that the extra features in the DOS, around 6 eV, would be hardly observable experimentally, being covered by the Ag(4*d*) bands which extend from 4 to 8 eV (Fig. 2, left panel; in LDA calculations the *d* bands come about 1 eV higher than they are experimentally). Similarly the predicted change in the DOS of the Ag4d band after oxidation would be covered by the photoemission from the Ag atoms of deeper layers or of clean surface regions. From experiment and theory we thus conclude that CO oxidation of O528 leads to the formation of a surface oxide phase with oxygen both above (O529) and

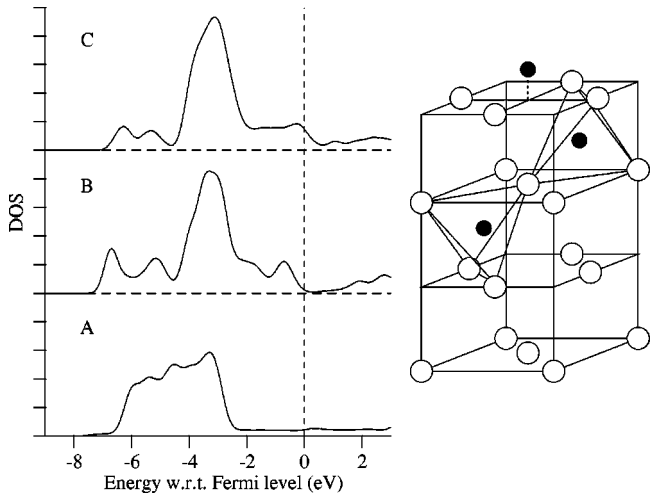

FIG. 3. Calculated total density of states for a slab of bare Ag(001) (a), bulk Ag_2O (b) and (c) for the model reported in the right-hand side with oxygen above and below the surface. Open circles are Ag atoms and filled circles oxygen atoms.

below the surface. The eventual evolution upon further CO exposure could not yet be reproduced by theory, since it involves more complex restructurings. Comparison with the DOS reported in Fig. 3(b) is however indicative of the formation of an Ag_2O-like phase.

Highlighted by the present investigation, we suggest that the occasional observation of CO adsorption for apparently clean Ag surfaces at 100 K$<T<$200 K (Refs. 8–10) was due to significant population of subsurface oxygen. The increased residence time of the CO molecules at the surface is expected to severely affect the kinetics of a Langmuir-Hinshelwood reaction such as CO oxidation. An increased reactivity of oxygen towards CO oxidation in presence of subsurface oxygen was recently reported also for O/Ru(0001).[18]

More recently CO adsorption was reported to induce segregation of Ni on Cu.[19] While the accumulation of foreign metal atoms at the surface is excluded in our case by XPS inspection, the mechanism responsible for oxygen segregation on Ag is most probably the same and is connected to the gain in chemical energy caused by the formation of CO-Ag-O_{sub} complexes. This mechanism is known to be responsible also for the, CO adsorption induced, segregation of oxygen in zeolites.[20]

According to van den Hoek *et al.*[21] the shift of the oxygen antibonding level towards the Fermi level, caused by the interaction of the oxygen adatoms with subsurface oxygen removes the activation barrier for the formation of EtO. While further experiments are needed for the verification of this hypothesis, we remark that a large concentration of subsurface oxygen is surely present in the industrial reaction conditions but is generally absent when the experiments are performed in UHV, especially as significant subsurface oxygen accumulation occurs only by CO-induced segregation. Our results provide therefore a rational explanation for the failure of the previous UHV experiments to detect significant EtO production and of why the chemists can activate the Ag powders by exposing them to gas mixtures containing either CO or C_2H_4.[4] As the reaction with O528 leads to total oxidation, the epoxidation of C_2H_4 involves most probably the less reactive oxygen moieties (characterized by larger $E_B[O(1s)]$ values) which are known to be stable up to high temperatures when O_2 is dosed at atmospheric pressure.[22]

In conclusion we have shown that (a) after the removal of O528 by CO oxidation subsurface oxygen, most probably in ocatahedral sites, stabilizes CO adsorption up to crystal temperatures above 160 K; (b) upon heating the crystal and allowing for surface mobility a surface oxide phase forms, which is stable up to 670 K and is characterized by an enhanced density of states near E_F; (c) the same oxide phase is fromed when dosing CO above room temperature on an oxygen precovered surface. The remarkable increase of the DOS at E_F signals the presence of oxygen adatoms particularly active for catalytical reactions.

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*Corresponding author: FAX: +390103622790, Email address: Rocca@fisica.unige.it

[1] R.J. Madix, in *Surface Reactions* (Springer-Verlag, Berlin, 1994).
[2] J.G. Serafin, A.C. Liu, and S.R. Seyedmonir, J. Mol. Catal. A: Chem. **131**, 157 (1998).
[3] R.B. Grant and R.M. Lambert, J. Catal. **92**, 364 (1985).
[4] V.I. Bukthyarov *et al.*, J. Catal. **150**, 268 (1994).
[5] M. Rocca *et al.*, Phys. Rev. B **69**, 213 (2000).
[6] A. Abrami *et al.*, Rev. Sci. Instrum. **66**, 1618 (1995).
[7] U. Burghaus and H. Conrad, Surf. Sci. **331-333**, 116 (1995).
[8] U. Burghaus *et al.*, Surf. Sci. **374**, 1 (1997).
[9] M. Canepa *et al.*, Chem. Phys. Lett. **177**, 123 (1991).
[10] M. Wittmann and J. Kuppers, Surf. Sci. **221**, L784 (1989).
[11] B.A. Sexton and R.J. Madix, Chem. Phys. Lett. **76**, 294 (1980).
[12] H.P. Bonzel, in *Landolt Börnstein, Adsorbate Covered Surfaces* (Springer-Verlag, Berlin, 2000).
[13] S. Krause *et al.*, Surf. Sci. **138**, 305 (1984).
[14] C. Backx *et al.*, Surf. Sci. **128**, 81 (1983); **104**, 300 (1981).
[15] G. te Velde and E.J. Baerends, Phys. Rev. B **44**, 7888 (1989).
[16] L.H. Tjeng, M.B.J. Meinders, and G.A. Sawatzky, Surf. Sci. **236**, 341 (1990).
[17] M.T. Czyzyk *et al.*, Phys. Rev. B **39**, 9831 (1989).
[18] A. Böttcher *et al.*, J. Phys. Chem. **103**, 6267 (1999).
[19] E. Nerlov and A. Chorkendorff, Catal. Lett. **54**, 171 (1998); J. Catal. **181**, 271 1999.
[20] D.H. Strome and K. Klier, J. Phys. Chem. **84**, 981 (1980); Langmuir **4**, 13 (1988).
[21] P.J. van den Hoek, E.J. Baerends, and R.A. van Santen, J. Phys. Chem. **93**, 6469 (1989).
[22] X. Bao *et al.*, Phys. Rev. B **54**, 2249 (1996).